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(54) Title: SILICONE ADHESIVES, ARTICLES, AND METHODS

(57) Abstract

The present invention provides silicone-based adhesives, preferably pressure sensitive adhesives, adhesive articles, and methods. Preferably, the articles are cover tapes for analytical receptacles, such as microtiter plates, microfluidic devices, and continuous multi-reservoir carriers, or other analytical receptacles or biosensors, for example. Typically, such analytical receptacles are used in bioanalytical applications and are designed for containing solids and fluids, including liquids, gases, powders, and gels, which may include biological samples or organic solvents, for example.

## SILICONE ADHESIVES, ARTICLES, AND METHODS

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### Field of the Invention

The invention relates to silicone adhesives, articles, and methods of making and using. The adhesives are particularly useful on articles such as cover tapes for analytical receptacles, such as microtiter plates, microfluidic devices, discrete or continuous multi-reservoir carriers, or other analytical receptacles, particularly those that are designed for holding a variety of liquids, in bioanalytical applications, for example.

### Background

15            Microtiter plates are well known for use in handling liquid materials in bioanalytical assays for multiple, rapid, low-volume analysis. A typical screening technique combines an assay plate, having multiple depressions or wells, with liquid handling hardware to provide a rapid, automated system of analysis. In a current, standard analytical system, each  
20          assay plate accommodates 96 wells, each well being addressable by suitably programmed hardware. The capacity of each of the 96 wells is about 0.2 milliliter (ml) to about 0.4 ml. Smaller capacity wells lead to assay plates that accommodate a larger number of samples. For example, assay plates containing 1536 wells, each with a capacity of less than 5 microliters ( $\mu$ l) are known.  
25          These plates, with increased sampling capability, have demonstrated usefulness in a variety of assays, including enzyme assays, receptor-ligand assays, and even cell based assays. The increased number of sample wells, per assay plate, demands increased precision of the hardware associated with analysis using these assay plates.

30            Liquid handling for bioanalytical applications, using assay plates of either the 96-well, 384-well, or the 1536-well variety, may be viewed as a

low tack adhesive tape is desirable to prevent the tape from sticking to rubber gloves commonly used in biological research, when applied to a microplate, for example, low adhesion of thick, elastic adhesive tapes is likely to cause a high evaporation rate and increase the incidence of cross-contamination during

5 storage and handling.

To increase cohesive strength and reduce contamination due to residual adhesive, silicone may be cured or crosslinked by catalysts such as peroxide or metallic salts at elevated temperatures. For example, benzoyl peroxide requires a cure temperature of more than 150°C for the catalyst to be 10 functional. Consequently, a backing with low melting or softening point, such as a polyethylene film, may be overly stretched or distorted dimensionally during curing. To prepare a curable silicone tape, one common practice is to coat curable silicones on a release liner consisting of a fluorosilicone coating and PET (polyethylene terephthalate) backing. The tape is then laminated with the 15 backings of low melting or softening point temperatures. Since release liners are commonly used to process and to protect silicone adhesive surfaces, it is important that the release force to separate the tape from the release liner be kept at a low level to minimize distortion of the tape backing, particularly when the release liner is removed during an automatic process.

20 U.S. Pat. No. 5,082,706 (Tangney) describes a silicone PSA/fluorosilicone release laminate having a release force of less than 7.7 N/dm (7 oz/in) from the fluorosilicone release layer and a peel adhesion of at least 46.4 N/dm (42.2 oz/in). This adhesive includes a tackifying resin (often referred to as an MQ resin) containing two structural units, one of which is R<sub>3</sub>SiO<sub>1/2</sub> 25 (often designated as M) and the other SiO<sub>4/2</sub> (often designated as Q). As discussed in The Handbook of Pressure-Adhesive Technology, 2<sup>nd</sup> Edition, (ed. D. Satas, 1989) p. 510, the peel adhesion of silicone pressure sensitive adhesives can be controlled by controlling the amount of tackifying resin. For example, increasing the amount of tackifying resin increases the peel adhesion; however,

example. As used herein, a substantially solvent-resistant cover tape, and particularly adhesive, is one that does not substantially swell or dissolve in the solvent used in the particular application and does maintain sufficient adhesion to the analytical receptacle.

5 In one embodiment, the present invention provides a silicone adhesive, preferably, a pressure sensitive adhesive, which is prepared from components including: (a) a polydiorganosiloxane having the general formula  $R^1R_2SiO(R_2SiO)_nSiR_2R^1$  and a number average molecular weight of at least 20,000, wherein each R is independently a monovalent hydrocarbon group, each  
10 R<sup>1</sup> is independently an alkenyl group, and n is an integer; (b) a polydiorganosiloxane having the general formula  $R^1R_2SiO(R_2SiO)_m(R^1RSiO)_nSiR_2R^1$  and a number average molecular weight of less than 20,000, wherein each R and R<sup>1</sup> is independently a monovalent hydrocarbon group, at least two R<sup>1</sup> groups are alkenyl groups, and m and n are  
15 integers the sum of which provide an alkenyl equivalent weight of about 250 to about 10,000; (c) an organopolysiloxane MQ resin which contains  $(R^2)_3SiO_{1/2}$  units and SiO<sub>2</sub> units in a molar ratio in the range of 0.6:1 to 1:1, wherein each R<sup>2</sup> is independently selected from the group of alkyl groups, alkenyl groups, or hydroxyl groups, wherein at least 95 mole percent of all R<sup>2</sup> groups are methyl  
20 groups; (d) an organohydrogenpolysiloxane free of aliphatic unsaturation having an average of at least 2 silicon-bonded hydrogen atoms in each molecule, in a quantity sufficient to provide from 1 to 40 silicon-bonded hydrogen atoms per alkenyl group in components (a) through (c); and (e) a Group VIIIB-containing catalyst in a quantity sufficient to provide 0.1 to 1,000 weight parts Group VIIIB  
25 metal for each one million weight parts of the combined quantity of components (a) through (d). Methods of making and methods of using such adhesives are also provided.

In another embodiment, the present invention provides an adhesive article that includes a substrate having disposed on at least one major

In yet another embodiment, the present invention provides an analytical receptacle that includes a surface and a cover tape adhered to the surface; wherein the cover tape includes a backing and an adhesive disposed on at least one major surface of the backing and in contact with the receptacle

5 surface, wherein the adhesive is prepared from components including: (a) a polydiorganosiloxane having the general formula  $R^1R_2SiO(R_2SiO)_nSiR_2R^1$  wherein each R is independently a monovalent hydrocarbon group, each R<sup>1</sup> is independently an alkenyl group and n is an integer; (b) an organopolysiloxane MQ resin which contains  $(R^2)_3SiO_{1.2}$  units and SiO<sub>2</sub> units in a molar ratio in the

10 range of 0.6:1 to 1:1, wherein each R<sup>2</sup> is independently selected from the group of alkyl groups, alkenyl groups, or hydroxyl groups, wherein at least 95 mole percent of all R<sup>2</sup> groups are methyl groups; (c) an organohydrogenpolysiloxane free of aliphatic unsaturation having an average of at least 2 silicon-bonded hydrogen atoms in each molecule, in a quantity sufficient to provide from 1 to

15 40 silicon-bonded hydrogen atoms per alkenyl group in component (a) and component (b) if present; and (d) a Group VIIIB-containing catalyst in a quantity sufficient to provide 0.1 to 1,000 weight parts Group VIIIB metal for each one million weight parts of the combined quantity of components (a) through (c); wherein the adhesive when disposed on a fluorosilicone-coated

20 polyethylene terephthalate release liner and a propylene/ethylene copolymer backing at a coating weight of 0.8 grams/154.8 cm<sup>2</sup> to form a laminate, and when adhered to a glass plate, displays a 180° release force of no greater than about 20 N/dm when measured at 30.5 cm/minute and room temperature.

The analytical receptacle can be in the form of a substantially continuous tape or it can be in discrete shapes and sizes, preferably with one or more reservoirs. For example, the analytical receptacle can be in the form of a microtiter plate, a microfluidic device comprising a substrate and one or more channels therein, or a substantially continuous polymeric strip (i.e., tape) comprising a plurality of reservoirs at predetermined intervals (preferably,

receptacle. Preferably, this results in producing individually sealed enclosures. Materials may be injected into or extracted from the closed reservoirs, through the cover tape, using suitable hypodermic-type needles, for example, if so desired. Preferred analytical receptacles can include one or more reservoirs.

- 5 They can be substantially continuous or discrete (i.e., noncontinuous) structures. For example, an analytical receptacle can be in the form of a microtiter plate that is conventionally used in bioanalytical methods. Alternatively, it can be a microfluidic device or continuous multi-reservoir carrier, for example, which can be cut into discrete (noncontinuous) pieces, if desired. Preferably,  
10 conventional analytical receptacles are made of polyolefins, polystyrene, and/or polycarbonate, for example, and more preferably, polypropylene and/or polystyrene.

A cover tape of the present invention, which acts as a sealing membrane, includes a silicone adhesive, preferably, a pressure sensitive silicone adhesive, disposed on a backing. Preferably, the backing is made of a transparent material to allow for photometric analysis and/or visual inspection.  
15 A cover tape of the present invention preferably adheres well to materials of which conventional analytical receptacles are made (preferably polyolefins, polystyrene, polycarbonate, or combinations thereof, and more preferably, polypropylene, polystyrene, or combinations thereof) and is preferably repositionable (i.e., the adhesive permits repeated cycles in which materials are alternatively bonded thereto and removed therefrom, while the adhesive is permanently retained on the backing of the adhesive article), but does not allow cross-contamination of sample materials in the individual reservoirs. Preferably,  
20 the cover tape maintains adhesion during high and low temperature storage (e.g., about -80°C to about 200°C) while providing an effective seal against sample evaporation (e.g., less than 5% loss within 24 hours as used in a analytical quantitative analysis setting). Suitable cover tapes of the present invention allow for puncture by needles, such as stainless steel needles, or plastic sampling

typically have excellent thermal and oxidative stability and a very broad service temperature range (i.e., a temperature range in which the adhesive is useful) of about -80°C to about 200°C. Silicone is also generally inert to a wide variety of polar chemicals and solvents, for example, water, methanol, ethanol,

5 acetonitrile/water, and DMSO commonly used in bioanalytical testing.

Furthermore, silicones are substantially biocompatible and are used in various medical devices. These properties make them excellent adhesives for use in, for example, cover tapes for analytical receptacles that are used in bioanalytical applications. However not all silicone adhesives in combination with all

10 backings have the appropriate balance of properties (e.g., peel force, release force, and tack).

A silicone adhesive laminate disclosed in U.S. Pat. No. 5,082,706 (Tangney) includes an addition-cured silicone pressure sensitive adhesive on an addition-cured fluorosilicone release coating. When thin backings are employed

15 in adhesive article constructions, it is desirable that upon separating the adhesive article (e.g., cover tape) from the release liner, release be sufficiently low that little if any permanent deformation of the backing occur. Thin backings (e.g., less than about 0.005 cm thick) and/or backings having low flexural modulus (e.g., polyolefins), deform easily. Thus, release forces required to separate

20 adhesive articles based on such backings need to be very low to avoid inducing permanent deformation or curl in the adhesive article.

Although the release force needed to separate the adhesive from the fluorosilicone release coating of U.S. Pat. No. 5,082,706 (Tangney), after it is cast onto and cured in contact with the release coating, is reported to have a

25 value of less than 200 grams per inch (7.7 N/dm), while at the same time displaying stable subsequent adhesiveness (46.4 N/dm from stainless steel) and stable subsequent tack, commercially available materials do not generally display sufficiently low release forces for many applications. For example, Dow Corning 7657 silicone adhesive displays a release force from a Rexam CLPET-

containing 10 carbon atoms; the molar ratio of M to Q units in the MQ resin is in the range of 0.6:1 to 1:1; and a Group VIIIB-containing metal catalyst.

Embodiments of the silicone adhesive of U.S. Pat. No. 5,082,706 that contain higher levels of the MQ resin typically display lower release values 5 from the fluorosilicone liner, without significantly detrimentally affecting the peel values from other substrates (generally, polyolefins, polystyrene, polycarbonate, for example, and preferably, polypropylene and polystyrene).

Preferably, the level of MQ resin (and other components of the adhesives described herein) can be adjusted to provide an adhesive, which when disposed on a fluorosilicone-coated polyethylene terephthalate release liner and a ethylene/propylene copolymer backing at a coating weight of 0.8 grams/154.8 cm<sup>2</sup> to form a laminate, and when the laminate is adhered to a glass plate, displays a 180° release force of no greater than about 20 N/dm, more preferably, no greater than about 15 N/dm, even more preferably, no greater than about 10 10 N/dm, and most preferably, no greater than about 5 N/dm, when measured at 15 30.5 cm/minute and room temperature (about 25°C to about 30°C). Preferably, the level of MQ resin (and other components of the adhesives described herein) can also be adjusted to provide an adhesive, which when disposed on a ethylene/propylene copolymer backing at a coating weight of 0.8 grams/154.8 20 cm<sup>2</sup> and adhered to a polypropylene plate, displays a 180° peel force of at least about 5 N/dm, more preferably, at least about 10 N/dm, and most preferably, at least about 15 N/dm, when measured at 30.5 cm/minute and room temperature (about 25°C to about 30°C). Preferably, the peel force is no greater than about 50 N/dm.

25 Suitable types and amounts of the various adhesive components described above are those that are disclosed in U.S. Pat. No. 5,082,706 (Tangney). Typically, the amount of MQ resin (i.e., one in which R<sup>2</sup> is an alkyl group) needed to achieve desired levels of release and peel forces will depend on

groups (such as vinyl, propenyl, hexenyl, etc., up to, for example, groups containing 10 carbon atoms), and m and n are integers the sum of which provide an alkenyl equivalent weight of about 250 to about 10,000; (c) an organopolysiloxane (designated as an MQ resin) which contains  $(R^2)_3SiO_{1/2}$  units (designated as M units) and SiO<sub>2</sub> units (designated as Q units) in a molar ratio in the range of 0.6:1 to 1:1, wherein R<sup>2</sup> is selected from the group of alkyl (such as methyl, ethyl, propyl, hexyl, etc., up to, for example, groups containing 10 carbon atoms), alkenyl (such as vinyl, propenyl, hexenyl, etc., up to, for example, groups containing 10 carbon atoms), or hydroxyl groups, wherein at least 95 mole percent of all R<sup>2</sup> groups are methyl groups; (d) an organohydrogenpolysiloxane free of aliphatic unsaturation having an average of at least 2 silicon-bonded hydrogen atoms in each molecule, in a quantity sufficient to provide from 1 to 40 silicon-bonded hydrogen atoms per alkenyl group in components (a) through (c); and (e) a Group VIIIB-containing catalyst in a quantity sufficient to provide 0.1 to 1,000 weight parts Group VIIIB metal for each one million weight parts of the combined quantity of components (a) through (d). Preferably, such compositions include both nonfunctional and functional MQ resins, particularly alkenyl-functional MQ resins.

Suitable polydiorganosiloxanes having the general formula R<sup>1</sup>R<sub>2</sub>SiO(R<sub>2</sub>SiO)<sub>n</sub>SiR<sub>2</sub>R<sup>1</sup> and a number average molecular weight of at least 20,000 are commercially available from sources such as Gelest Inc., Tullytown, PA. Examples are disclosed in U.S. Pat. No. 5,082,706 (Tangney). For particularly preferred embodiments, the molecular weight is preferably at least about 50,000, more preferably, at least about 100,000, and most preferably, at least about 250,000.

Suitable polydiorganosiloxane of the general formula R<sup>1</sup>R<sub>2</sub>SiO(R<sub>2</sub>SiO)<sub>m</sub>(R<sup>1</sup>RSiO)<sub>n</sub>SiR<sub>2</sub>R<sup>1</sup> and a number average molecular weight of less than 20,000 are commercially available from sources such as Gelest Inc. Preferred such materials have an alkenyl equivalent weight (as a result of the

Midland, MI and General Electric Silicones, Waterford, NY. Examples are disclosed in U.S. Pat. No. 5,082,706 (Tangney).

Such silicone adhesives are prepared by addition-cure chemistry and typically involve the use of a platinum or other Group VIIIB (i.e., Groups 8, 5 9, and 10) metal catalysts, typically, hydrosilation catalysts, to effect the curing of the silicone adhesive. Reported advantages of addition-cured silicone adhesives include reduced viscosity as compared to silicone adhesives prepared via condensation chemistry, higher solids content, stable viscosity with respect to time, and lower temperature cure. Methods of preparation are disclosed in 10 U.S. Pat. No. 5,082,706 (Tangney).

The adhesive composition may include other additives to adjust for desired properties. For example, pigment may be added as colorant; conductive compounds may be added to make an adhesive surface electrically conductive or antistatic; antioxidants and bacteriastatic agents may be added; 15 light absorbers may be added to block certain wavelengths from passing through the article; or inhibitors may be added to extend adhesive pot life, thus avoiding premature gelation of the adhesive coating solution. Examples of such additives are commercially available from various sources and are disclosed in U.S. Pat. No. 5,082,706 (Tangney), as are desired amounts.

20 The adhesive composition can be applied to appropriate release liners by a wide range of processes, including, solution coating, solution spraying, etc., to make adhesive/release liner laminates, preferably at a coating weight of about 0.2 grams/154.2 cm<sup>2</sup> to about 2.4 grams/154.2 cm<sup>2</sup>. Typically, it is applied to a thermally resistant substrate, such as polyethylene terephthalate 25 coated with a fluorosilicone release material (such as that disclosed in U.S. Pat. No. 5,082,706 and commercially available from Rexam Release, Bedford Park, IL) to form an adhesive/release liner laminate. The adhesive transfer tape is then laminated to a desired substrate, such as biaxially oriented polyethylene or high density polyethylene, to form an adhesive tape, particularly a cover tape for

The analytical receptacles to which the cover tapes can be applied include a wide variety of articles. Preferably, the analytical receptacles include at least one surface having one or more reservoirs therein. For example, a suitable analytical receptacle to which a cover tape of the present invention can be applied includes a microtiter plate, which is typically a plastic plate containing a number of small flat-bottomed wells arranged in rows. Another example is a tape that includes a substrate coated with a gel having a plurality of separate adjacent tracks thereon, as disclosed in U.S. Pat. No. 3,551,295 (Dyer).

- 5 Other analytical receptacles include microfluidic devices that 10 include a substrate and one or more channels therein. Such a structure, which includes a body structure and at least one microscale channel disposed therein, is disclosed in U.S. Pat. No. 5,842,787 (Kopf-Sill et al.). Yet another such structure, which has a groove recessed in a flat substrate and defines a 15 microfluidic channel system, is disclosed in U.S. Pat. No. 5,443,890 (Ohman). Yet another such structure, which includes a substrate with microstructures fabricated therein, is disclosed in U.S. Pat. No. 5,804,022 (Kaltenbach et al.).

Another type of analytical receptacle includes a substantially continuous polymeric strip formed to have wall portions defining a series of identical reservoirs at predetermined, preferably, uniformly spaced, intervals 20 along its length, which reservoirs can have a variety of shapes. For example, the reservoirs may comprise rectangular or generally "I" or "T" shapes in the plane of the strip, and may have flat or rounded bottoms as desired. Such receptacles are disclosed, for example, in U.S. Pat. No. 4,883,642 (Bisconte). Others are disclosed in U.S. Pat. No. 5,729,963 (Bird), which are designed for carrying 25 electrical parts, but can be modified for use as analytical receptacles.

These analytical receptacles can be formed from a variety of materials, including, polyethylene, polystyrene, polypropylene, polycarbonate, which can be carbon-black or TiO<sub>2</sub> filled, transparent, translucent, or opaque.

tester and recorded. The experiment was repeated three times and average value reported in N/dm.

- Cross Contamination Test:** In a polystyrene 96-well microplate (available from Nalge International Corp, Naperville, IL)
- 5 alternating wells were filled with approximately 50  $\mu$ l of a red colorant solution (MERTHIOLATE, supplied by Eli Lilly, approximately 1:50 dilution in water) and the openings of the wells of the microplate were covered by the sample adhesive cover tapes. The covered plate was subsequently inverted and shaken several times. The wells in the plate were then visually observed to determine if  
10 the indicator solution had migrated to an adjacent well.

- Solvent Resistance Test:** Sample adhesive tapes were adhered to an aluminum plate with 6 wells, each well having a dimension of 0.6 cm diameter and 0.6 cm depth. Prior to application of the cover tape, DMSO (50  $\mu$ l) was filled in each well and allowed to dwell for 24 hours in the tape-covered  
15 wells. The tapes were subsequently inspected visually for evidence of swelling or dissolution.

- Extractables Test:** Samples (4 cm x 5 cm) of each adhesive cover tape were soaked in 5 ml of water or dimethyl sulfoxide (DMSO) for 24 hours. The sample adhesive tapes were also exposed to vapor phase contact  
20 with the solvents in the wells of the sample adhesive tape-covered aluminum plate described above for 7 days. The extracts were examined by gas chromatography/mass spectroscopy (GC/MS) using a Finnigan "Magnum" GC/ion trap mass spectrometer (available from Thermoquest Corporation., San Jose, CA) equipped with a model ZB-5 column (30 meters in length, 0.25 mm  
25 inner diameter, 0.1  $\mu$ m film (available from Phenomenex Torrence, CA), a 4-ml Atas Optic 2 injector (available from Atas, Cambridge Cambridgeshire, United Kingdom), and a Finnegan scanning electron impact detector available from Thermoquest Corporation, San Jose, CA (electron impact scan range from 31 Daltons to 550 Daltons. The Atas injector was operated in a cold split, multi-

vinyldimethylsiloxane terminated polydimethylsiloxane with molecular weight approximately 500,000 and 56 wt % nonreactive MQ tackifying resin) with xylene as the diluent. Additional amounts of the same nonreactive MQ tackifying resin were added by the manufacturer to the Dow Corning 7657 adhesive to provide adhesive solutions 7657-2, 7657-4, 7657-6, and 7657-8 containing 58, 60, 62, and 64 wt % MQ respectively. Toluene (available from Worum Chemical Company, St. Paul, MN) was added to each formulation to provide the adhesive at 40 wt % solids content for ease of coating.

Dow Corning (Dow Corning Corporation, Midland, MI) SYL-  
10 OFF 7615 release modifier (designated as 7615) containing approximately 40 wt % dimethylvinylated and trimethylated silica; 57 wt % dimethylsiloxane, dimethylvinyl terminated with a degree of polymerization of 25; 1 wt % tetra(trimethylsiloxy) silane; 1 wt % of a Dow Corning proprietary ester; and a platinum-containing catalyst.

15 Dow Corning SYL-OFF 7678 crosslinker (designated as 7678) containing dimethylsiloxane methylhydrogensiloxane copolymer.

Dow Corning SYL-OFF 4000 catalyst (designated as 4000) containing dimethylvinyl terminated polydimethylsiloxane, tetramethyldivinyldisiloxane, and a platinum siloxane complex.

20

### Formulations

Adhesive Composition A: 250 parts of Dow Corning 7657 silicone base adhesive at 40% solids in toluene/xylene, and 1 part of SYL-OFF 4000 catalyst.

25 Adhesive Composition B: 250 parts of Dow Corning 7657-2  
silicone base adhesive at 40% solids in toluene/xylene, and 1 part of SYL-OFF  
4000 catalyst.

copolymer (PP-PE) film (BPI Code #26379-3, Bloomer Plastics Inc., Bloomer, WI) by passing the adhesive/release liner laminate and embossed tape backing through a nip roll.

- The peel force test and release force test were measured on each 5 of the prepared samples and reported in Tables 1-5. The results suggest that there is little effect on the peel forces of the silicone tapes when 0-20 parts of silicone modifier were added to the silicone adhesive. Surprisingly, the results show that addition of silicone modifier serves to decrease release force without adversely affecting peel adhesion.

10

Table 1

Adhesive Composition A with 0, 5, 10, 15, and 20 parts of Modifier 7615			
Example	Modifier 7615	Peel Force (N/dm)	Release Force (N/dm)
1	0 part	24.6	7.1
2	5 parts	22.0	6.7
3	10 parts	21.2	4.4
4	15 parts	21.5	2.1
5	20 parts	22.5	1.5

Table 4

Adhesive Composition D with 0, 5, 10, 15, and 20 parts of Modifier 7615			
Example	Modifier 7615	Peel Force (N/dm)	Release Force (N/dm)
16	0 part	20.9	0.4
17	5 parts	22.3	0.3
18	10 parts	29.8	0.2
19	15 parts	30.3	0.2
20	20 parts	26.7	0.2

5

Table 5

Adhesive Composition E with 0, 5, 10, 15, and 20 parts of Modifier 7615			
Example	Modifier 7615	Peel Force (N/dm)	Release Force (N/dm)
21	0 part	4.8	0.08
22	5 parts	8.7	0.09
23	10 parts	4.2	0.03
24	15 parts	7.0	0.04
25	20 parts	8.5	0.05

Formulations

Master batches of low molecular weight vinyl-substituted polydiorganosiloxanes ("vinyl-fluid" having varying degrees of polymerization) were prepared according to the following formulations.

5

Master Batch	Vinyl Fluid	Vinyl Fluid Amount (g)	MQ resin solution (g)	SYL-OFF 7678 crosslinker (g)	2EHHM (g)
A	A	21.0	46.4	2.1	0.17
B	B	19.1	39.8	0.72	0.15
C	C	19.3	39.8	0.49	0.15
D	D	19.5	39.8	0.30	0.15
E	E	19.6	39.8	0.21	0.15
F	F	19.7	39.8	0.11	0.15

For each of the following examples, the proper amount of each Master Batch as indicated in Tables 6-11 was mixed with 50 grams of the 40% solids Dow Corning 7657 and 0.2 gm of SYL-OFF 4000. A tumbling roller was used for 2-4 hours to insure uniform mixing prior to coating.

The resulting adhesive solutions were applied on a release liner (CLPET-6J/000 transfer liner from Rexam Release, Bedford Park, IL) and coated, dried, and cured as in Examples 1-25, with the exception that oven zones 1, 2, and 3 were set at temperatures of 125°C, 149°C, and 149°C, respectively. The adhesive/release liner laminate was then laminated on a tape backing, BOPP (biaxially oriented polypropylene film) available from 3M Company, St. Paul, MN under the trade name SCOTCHPRO having a thickness of 31  $\mu\text{m}$  (1.2 mils). The BOPP tape backing was corona-treated to enhance bonding of the silicone

Table 7

5. Coating Formulation with Vinyl Fluid B (DP = 67)

Example	Master Batch	Master Batch Amount (g)	Amount of Vinyl Fluid B in Master Batch B (g)	Peel Force from PP (N/dm)	Release Force (N/dm)
32	B	7.96	2.543	28.9	16.6
33	B	10.61	3.391	25.9	11.4
34	B	13.27	4.239	22.5	8.5
35	B	15.92	5.087	21.2	6.7

10

Table 8

Coating Formulation with Vinyl Fluid C (DP = 101)

Example	Master Batch	Master Batch Amount (g)	Amount of Vinyl Fluid C in Master Batch C (g)	Peel Force from PP (N/dm)	Release Force (N/dm)
36	C	7.96	2.574	23.7	24.9
37	C	10.61	3.432	27.4	16.8
38	C	13.27	4.291	24.8	12.8
39	C	15.92	5.149	26.3	10.8

Table 11  
Coating Formulation with Vinyl Fluid F (DP = 459)

Example	Master Batch	Master Batch Amount (g)	Amount of Vinyl Fluid F in Master Batch F (g)	Peel Force from PP (N/dm)	Release Force (N/dm)
C2	F	7.96	2.625	31.8	37.0
C3	F	10.61	3.500	30.7	34.3
C4	F	13.27	4.375	28.8	35.3
C5	F	15.92	5.250	28.8	30.3

### 5 Examples 48-49 and Comparatives C6-C11

The silicone adhesive composition of Example 13 on a release liner (CLPET-6J/000 transfer liner from Rexam Release Corporation, Bedford Park, IL) was laminated with the following backings.

Example 48 used an embossed high density polyethylene 10 designated as PE (Product No. B100NA from Bloomer Plastics, Bloomer, WI). The embossed film thickness was 101.6  $\mu\text{m}$  (4 mils).

Example 49 used a biaxially-oriented polypropylene having a thickness of 30.5  $\mu\text{m}$  (1.2 mil) and designated as BOPP available by the trade designation SCOTCHPRO from 3M Company, St. Paul, MN.

15 In a polystyrene 96-well microplate (available from Nalge Nunc International Corp, Naperville, IL) alternating wells were filled with approximately 50  $\mu\text{l}$  of a red colorant solution (MERTHIONATE, supplied by Eli Lilly, approximately 1:50 dilution in water) and the openings of the wells of the microplate were covered by the sample adhesive cover tapes of Examples 48 20 and 49. The covered plate was subsequently inverted and shaken several times.

Table 12  
DMSO Resistance of Silicone Tapes and Comparative Tapes

Example	Tape Backing	Adhesion in DMSO (24 hours)	Residue 22 G Needle
48	HDPE	Ok*	No residue visible
49	BOPP	Ok*	No residue visible
C6	SJ 3101	Swollen, lost adhesion	No residue visible
C7	THINSEAL	Swollen, lost adhesion	No residue visible

\*no noticeable change of adhesion.

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Table 13 reports the extraction data obtained in the Extractables Test utilizing the GC/MS conditions listed above with several common solvents utilized within a typical bioanalytical lab when preparing sample that would be introduced to a multi-well aluminum plate and covered. Samples of the tapes 10 were placed in DMSO, water and 80/20 acetonitrile/water mixture for 24 hours. Any extractable material was analyzed with GC/MS. The results indicated that no material was extracted from any of these tapes.

Comparative 8 was Corning cover tape (product number 3095) commercially available from Corning Corp., Corning, NY. Comparative 9 was 15 product number 62367 cover tape available from Zymark Corp., Hopkinton, MA. Comparative 10 was Costar product number 6569 cover tape available from Corning Costar Corp., Acton, MA. Comparative 11 was Ultra-Plate cover tape available from Sagian Corporation, Indianapolis, IN. Each of these cover tape samples were used as received. The results demonstrate a significant value 20 of the present invention is the ability of cover tapes of the present invention to resist commonly used solvents in bioanalytical applications.

Table 14

Evaporation Rates of Water in 24 Hours on a Perkin Elmer PCR 96-Well Plates

Example	Samples	Evaporation/24 hr
42	BOPP with silicone PSA	~3%
Comp 12	Robbins (CYCLESEAL) 30 mils Thick, low peel	~25%

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Evaporation Rates of Example 50 and Comp. 13-15

Example 50 utilized the adhesive of Example 42 and a 3-layer (A/B/A) coextruded film for the adhesive tape backing, where outerlayer A (thickness = 7 microns) was FINA polypropylene #3825 (available from FINA Oil & Chemical Co., Dallas, TX) and B is KRATON G1657 (available from Shell Chemical, Houston, TX) (thickness = 63 microns). The films were prepared on a coextrusion line using a Cloeren (Orange, Texas) ABBBC feedblock. The B Layer (elastic core) was split into three layers in the feedblock, recombined and sandwiched between the two skin layers to form the three-layer coextruded film. The A Layer (skin 1) was cast against a rubber nip roll. The C Layer (skin 2) was cast against a patterned steel chill roll. Extruder A (skin 1) was a 2.5-inch single screw (24:1 L/D) manufactured by David Standard Corporation (Pawcatuck, CT). Extruder B (elastic core) was a 2.5-inch single screw (32:1) manufactured by Extruders Inc. and Extruder C (skin 2) was a 1.5-inch single screw (24:1 L/D) manufactured by David Standard.

Comparative Examples 13 and 14 were commercially available adhesive tapes. Aluminum adhesive tape (Comp. 13, from Marsh Biomedical Products, Inc., Rochester, NY) and a PET adhesive tape (Comp. 14, trade name

Table 15  
Effect of A Septum Tape Backing on the Evaporation Rates of Some  
Commonly Used Solvents

Example	Solvents	Evaporation/hr
50	Acetonitrile: Water (84:16 by wt).	0.12%
50	Water	0.02%
50	DMSO	-0.02%
Comp 13	Acetonitrile: Water (84:16 by wt).	0.75%
Comp 14	Acetonitrile: Water (84:16 by wt).	1.10%
Comp 15*	Acetonitrile: Water (84:16 by wt).	29%

\* No cover tape

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#### Peel Force of Cover Tapes from Nitrile Rubber

- Peel force of adhesive tapes from a nitrile rubber surface (type: N-DEX 60005 PFM powders free, Best Manufacturing Co., Menio, GA) were measured using the Peel Force Test described above, except a portion of a nitrile rubber glove was adhered to the polypropylene plate with SCOTCH tape #411 (3M Company, St. Paul, MN). The data is shown in Table 16 for the cover tapes of Examples 11-15 and Comparative 14. The silicone tapes in this invention have very low peel adhesion to the commonly used rubber gloves.
- Furthermore, the silicone tapes have very low tack when touched with fingers or rubber gloves.

WHAT IS CLAIMED IS:

1. An adhesive prepared from components comprising:

(a) a polydiorganosiloxane having the general formula

$R^1R_2SiO(R_2SiO)_nSiR_2R^1$  and a number average molecular weight of  
5 at least 20,000, wherein each R is independently a monovalent  
hydrocarbon group, each  $R^1$  is independently an alkenyl group, and n  
is an integer;

(b) a polydiorganosiloxane having the general formula

$R^1R_2SiO(R_2SiO)_m(R^1RSiO)_nSiR_2R^1$  and a number average molecular  
10 weight of less than 20,000, wherein each R and  $R^1$  is independently a  
monovalent hydrocarbon group, at least two  $R^1$  groups are alkenyl  
groups, and m and n are integers the sum of which provide an alkenyl  
equivalent weight of about 250 to about 10,000;

(c) an organopolysiloxane MQ resin which contains  $(R^2)_3SiO_{1/2}$  units and  
15  $SiO_2$  units in a molar ratio in the range of 0.6:1 to 1:1, wherein each  
 $R^2$  is independently selected from the group of alkyl groups, alkenyl  
groups, or hydroxyl groups, wherein at least 95 mole percent of all  
 $R^2$  groups are methyl groups;

(d) an organohydrogenpolysiloxane free of aliphatic unsaturation having  
20 an average of at least 2 silicon-bonded hydrogen atoms in each  
molecule, in a quantity sufficient to provide from 1 to 40 silicon-  
bonded hydrogen atoms per alkenyl group in components (a) through  
(c); and

(e) a Group VIIIB-containing catalyst in a quantity sufficient to provide  
25 0.1 to 1,000 weight parts Group VIIIB metal for each one million  
weight parts of the combined quantity of components (a) through (d).

2. The adhesive of claim 1 wherein the organopolysiloxane MQ resin  
includes both nonfunctional and functional MQ resins.

11. The adhesive article of claim 10 wherein the organopolysiloxane MQ resin includes both nonfunctional and functional MQ resins
- 5 12. The adhesive article of claim 10 further comprising a release liner disposed on the adhesive.
- 10 13. The adhesive article of claim 10 wherein the adhesive when disposed on a fluorosilicone-coated polyethylene terephthalate release liner and a propylene/ethylene copolymer backing at a coating weight of 0.8 grams/154.8 cm<sup>2</sup> to form a laminate, and when adhered to a glass plate, displays a 180° release force of no greater than about 20 N/dm when measured at 30.5 cm/minute and room temperature.
- 15 14. The adhesive article of claim 13 wherein the adhesive displays a release force of no greater than about 5 N/dm.
15. The adhesive article of claim 10 wherein the adhesive when disposed on a propylene/ethylene copolymer backing at a coating weight of 0.8 grams/154.8 cm<sup>2</sup> and adhered to a polypropylene plate displays a 180° peel force of at least about 5 N/dm when measured at 30.5 cm/minute and room temperature.
- 20 16. The adhesive article of claim 10 wherein the backing comprises a puncturable material.
- 25 17. The adhesive article of claim 10 wherein the adhesive is a pressure sensitive adhesive.

25. The analytical receptacle of claim 18 further comprising one or more reservoirs including a liquid therein during use.
- 5 26. The analytical receptacle of claim 25 wherein the liquid comprises dimethyl sulfoxide, water, acetonitrile/water, methanol, ethanol, or mixtures thereof.
- 10 27. The analytical receptacle of claim 18 comprising a microtiter plate.
28. The analytical receptacle of claim 18 comprising a microfluidic device comprising a substrate and one or more channels therein.
- 15 29. The analytical receptacle of claim 18 comprising a substantially continuous polymeric strip comprising a plurality of reservoirs at predetermined intervals along its length.
30. The analytical receptacle of claim 29 wherein the reservoirs are uniformly spaced.

the receptacle surface, wherein the adhesive is prepared from components comprising:

(e) a polydiorganosiloxane having the general formula

$R^1R_2SiO(R_2SiO)_nSiR_2R^1$  wherein each R is independently a monovalent hydrocarbon group, each R<sup>1</sup> is independently an alkenyl group and n is an integer;

(f) an organopolysiloxane MQ resin which contains  $(R^2)_3SiO_{1/2}$  units and SiO<sub>2</sub> units in a molar ratio in the range of 0.6:1 to 1:1, wherein each R<sup>2</sup> is independently selected from the group of alkyl groups, alkenyl groups, or hydroxyl groups, wherein at least 95 mole percent of all R<sup>2</sup> groups are methyl groups;

(g) an organohydrogenpolysiloxane free of aliphatic unsaturation having an average of at least 2 silicon-bonded hydrogen atoms in each molecule, in a quantity sufficient to provide from 1 to 40 silicon-bonded hydrogen atoms per alkenyl group in component (a) and component (b) if present; and

(h) a Group VIIIB-containing catalyst in a quantity sufficient to provide 0.1 to 1,000 weight parts Group VIIIB metal for each one million weight parts of the combined quantity of components (a) through (c);

wherein the adhesive when disposed on a fluorosilicone-coated polyethylene terephthalate release liner and a propylene/ethylene copolymer backing at a coating weight of 0.8 grams/154.8 cm<sup>2</sup> to form a laminate, and when adhered to a glass plate, displays a 180° release force of no greater than about 20 N/dm when measured at 30.5 cm/minute and room temperature.

34. A method of sealing an analytical receptacle comprising applying a cover tape comprising a backing and the adhesive of claim 1 disposed on at least one major surface thereof.

# INTERNATIONAL SEARCH REPORT

Interr. Application No  
PCT/US 99/09945

**A. CLASSIFICATION OF SUBJECT MATTER**  
IPC 7 C09J183/07 B65B9/04

According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C09J B65B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 581 539 A (GEN ELECTRIC) 2 February 1994 (1994-02-02) claims 1,3,4,9 page 5, line 31 -page 6, line 9 ---	1-3
A	US 5 082 706 A (TANGNEY THOMAS J) 21 January 1992 (1992-01-21) cited in the application claim 1 ---	1
A	US 5 721 136 A (TITCOMB PAUL ET AL) 24 February 1998 (1998-02-24) cited in the application claims 1-14 ---	1 -/-

Further documents are listed in the continuation of box C.

Patent family members are listed in annex.

\* Special categories of cited documents :

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- "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
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# INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

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Patent document cited in search report	Publication date	Patent family member(s)			Publication date
EP 0581539	A 02-02-1994	CA JP	2101708 A 6166861 A		31-01-1994 14-06-1994
US 5082706	A 21-01-1992	AT CA EP IE JP KR	86286 T 2002073 A 0370689 A 62700 B 2189383 A 141486 B		15-03-1993 23-05-1990 30-05-1990 22-02-1995 25-07-1990 15-06-1998
US 5721136	A 24-02-1998		NONE		
US 5729963	A 24-03-1998	US CN DE DE EP JP WO	5648136 A 1190524 A 69601802 D 69601802 T 0838137 A 11509163 T 9703545 A		15-07-1997 12-08-1998 22-04-1999 04-11-1999 29-04-1998 17-08-1999 30-01-1997
EP 0506372	A 30-09-1992	US CA DE DE JP	5466532 A 2061973 A 69206457 D 69206457 T 5098240 A		14-11-1995 27-09-1992 18-01-1996 11-07-1996 20-04-1993